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<b>(21) International Application Number:</b> PCT/EP97/00996 <b>(22) International Filing Date:</b> 27 February 1997 (27.02.97)  <b>(30) Priority Data:</b> 08/608,266      28 February 1996 (28.02.96)      US  <b>(71) Applicant:</b> AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).  <b>(72) Inventor:</b> BRIGHT, Danielle, Angrand; 21 Zabela Drive, New York, NY 10956 (US).  <b>(74) Agent:</b> SCHALKWUJ, Pieter, Cornelis; Akzo Nobel N.V., Patent Dept. (Dept. APTA), P.O. Box 9300, NL-6800 SB Arnhem (NL).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>
<b>(54) Title:</b> 1,4-CYCLOHEXANEDIMETHANOL BIS(DIARYL PHOSPHATE)S  <b>(57) Abstract</b>  Novel flame retardant compounds for polymers, the 1,4-cyclohexanedimethanol bis(diphenyl phosphate)s, can be synthesized by reacting 1,4-cyclohexanedimethanol and a diphenyl halophosphate, such as diphenyl chlorophosphate, in the presence of a catalyst, such as magnesium chloride, in an appropriate solvent, such as hexane.		

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1,4-CYCLOHEXANEDIMETHANOL BIS(DIARYL PHOSPHATE)SBackground of the Invention

5 The prior art discloses a wide variety of diphosphate flame retardant compounds which contain two phosphate groups (often containing two phenyl substituents each) linked together by a bridging group -O-R-O-, where R comprises an arylene or alkylene group. Certain disclosures exist which include cyclohexylene as a possible alkylene group for R, including U.S. Patent No. 3,869,526 to M. Combey  
 10 et al. (see Col. 1, line 27) and U.S. Patent No. 4,343,732 to T. Zama et al. (see Col. 3, lines 52-53).

Summary of the Invention

15 The present invention relates to 1,4-cyclohexanedi-methanol bis(diaryl phosphate)s, which are useful as flame retardant compounds for polymers. This class of compound can be synthesized by reacting 1,4-cyclohexanedimethanol and a diaryl halophosphate, such as diphenyl chloro-phosphate, in the presence of a catalyst, such as magnesium chloride, either with or without an appropriate  
 20 solvent, such as hexane.

Description of Preferred Embodiments

The term "1,4-cyclohexanedimethanol bis(diaryl phosphate)s" as used herein is  
 25 intended to cover a novel class of diphosphate flame retardant compounds of the general formula



where Ar is either unsubstituted or substituted (e.g., lower alkyl substituted, halo, or alkoxy) aryl group (e.g., phenyl), A is a hydrocarbylene-containing bridging group of the formula  $\text{CH}_2\text{-C}_6\text{H}_4\text{-CH}_2$  and is derived from 1,4-cyclohexanedimethanol. A preferred compound is one containing unsubstituted phenyl as Ar, namely, 1,4-cyclohexanedimethanol bis(diphenyl phosphate).

The subject compounds can be easily formed by the reaction of 1,4-cyclohexanedimethanol and the desired diphenyl halophosphate in the presence of a catalyst in an appropriate solvent at elevated temperatures of from about 90 °C to about 150 °C, preferably, in a ratio of one mole of cyclohexanedimethanol to two moles of diaryl phosphate.

The diphenyl moiety on the selected diphenyl halophosphate reagent can be either unsubstituted or can be substituted, e.g., with one or more lower alkyl groups, halo groups, or alkoxy groups depending upon the type of product desired. The halo- moiety in this reagent can be either chloro or bromo with the former being preferred.

The solvent medium which is used can be, for example, an aliphatic solvent, such as heptane, or an aromatic solvent, such as toluene.

The catalyst that is used can be a Lewis acid catalyst such as magnesium chloride, aluminum chloride, titanium tetrachloride, zinc dichloride, and the like, in an amount of from about 0.05% to about 0.5%, by weight of the reactants, in a particularly preferred embodiment.

The following Examples further illustrate this invention and its characteristics.

EXAMPLE 1

5 This Example illustrates the synthesis of 1,4-cyclohexanedimethanol bis(diphenyl phosphate).

The following reagents and solvent were heated to reflux: 1,4-cyclohexanedimethanol (0.25 mole, 36.0 gm); diphenyl chlorophosphate (0.5 mole, 134.3 gm); magnesium chloride (250 mg); and hexane (34gm, 52 ml). The progress of the reaction was monitored by infrared spectroscopy. After about  
10 four and one half hours, the reaction was completed, and 150 ml of methanol was added to the reaction medium. The desired product crystallized from the reaction medium. After filtration, washing and drying, there was left 124.9 gm of a white solid (82.2% yield, over 90% purity by liquid chromatography) having a melting point of 70-75°C. The structure of the 1,4-cyclohexanedimethanol  
15 bis(diphenyl phosphate) product was confirmed by proton and  $^{31}\text{P}$  nmr.

**EXAMPLE 2**

In this Example, 94.4 parts by weight of high impact strength polystyrene (HIPS) and 5.6 parts by weight of the 1,4-cyclohexane-dimethanol bis(diphenyl phosphate) product from Example 1 were compounded and extruded. The  
5 Limiting Oxygen Index (LOI) of the piece was 20.5 as compared to 18 for a HIPS sample not containing the flame retardant additive.

The foregoing Example should not be construed in a limiting sense since it is  
10 intended to merely recite certain embodiments of the claimed invention. The scope of protection sought is set forth in the claims which follow.

What is Claimed:

1. 1,4-cyclohexanedimethanol bis(diaryl phosphate)s.
- 5     2. 1,4-cyclohexanedimethanol bis(diaryl phosphate).
3. Compounds as claimed in Claim 1 wherein the diaryl moieties are unsubstituted.
- 10    4. Compounds as claimed in Claim 1 wherein the diaryl moieties are substituted with at least one substituent selected from the group consisting of lower alkyl, halo, and alkoxy.
- 15    5. A compound as claimed in Claim 2 wherein the diaryl moieties are unsubstituted.
6. A compound as claimed in Claim 2 wherein the diaryl moieties are substituted with at least one lower alkyl group.

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## AMENDED CLAIMS

[received by the International Bureau on 28 July 1997 (28.07.97);  
original claims 1-6 replaced by new claims 1-7 (1 page)]

1. A composition comprising a polymer and a bisphosphate, characterized in that the bisphosphate is a 1,4-cyclohexanedimethanol bis(diaryl phosphate).
2. A composition according to claim 1, characterized in that the aryl group is unsubstituted.
3. A composition according to claim 1, characterized in that the aryl group is substituted with at least one substituent selected from the group consisting of lower alkyl, halo, and alkoxy.
4. A composition according to any one of the preceding claims, characterized in that the aryl group is a phenyl group.
5. 1,4-cyclohexanedimethanol bis(diaryl phosphate), characterized in that the aryl group is unsubstituted.
6. 1,4-cyclohexanedimethanol bis(diaryl phosphate) according to claim 1, characterized in that the aryl group is a phenyl group.
7. The use of a 1,4-cyclohexanedimethanol bis(diaryl phosphate) as a flame retardant.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 97/00996

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07F9/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 286 253 A (EASTMAN KODAK COMPANY) 12 October 1988 see compound no. I-11, page 4, see claim 5 ---	1
A	EP 0 613 902 A (AKZO NOBEL N.V.) 7 September 1994 see formula, page 2 ---	1
A	DE 26 25 878 A (MONSANTO CO.) 23 December 1976 see examples 5-8 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

information on patent family members

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